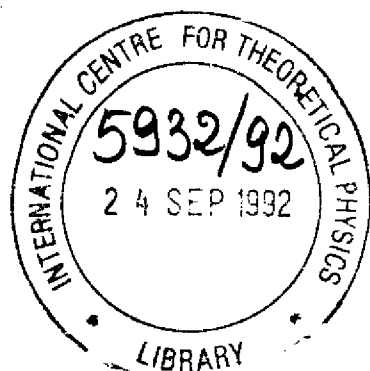# INTERNATIONAL CENTRE FOR
THEORETICAL PHYSICS

MELTING AND LIQUID STRUCTURE OF POLYVALENT METAL HALIDES

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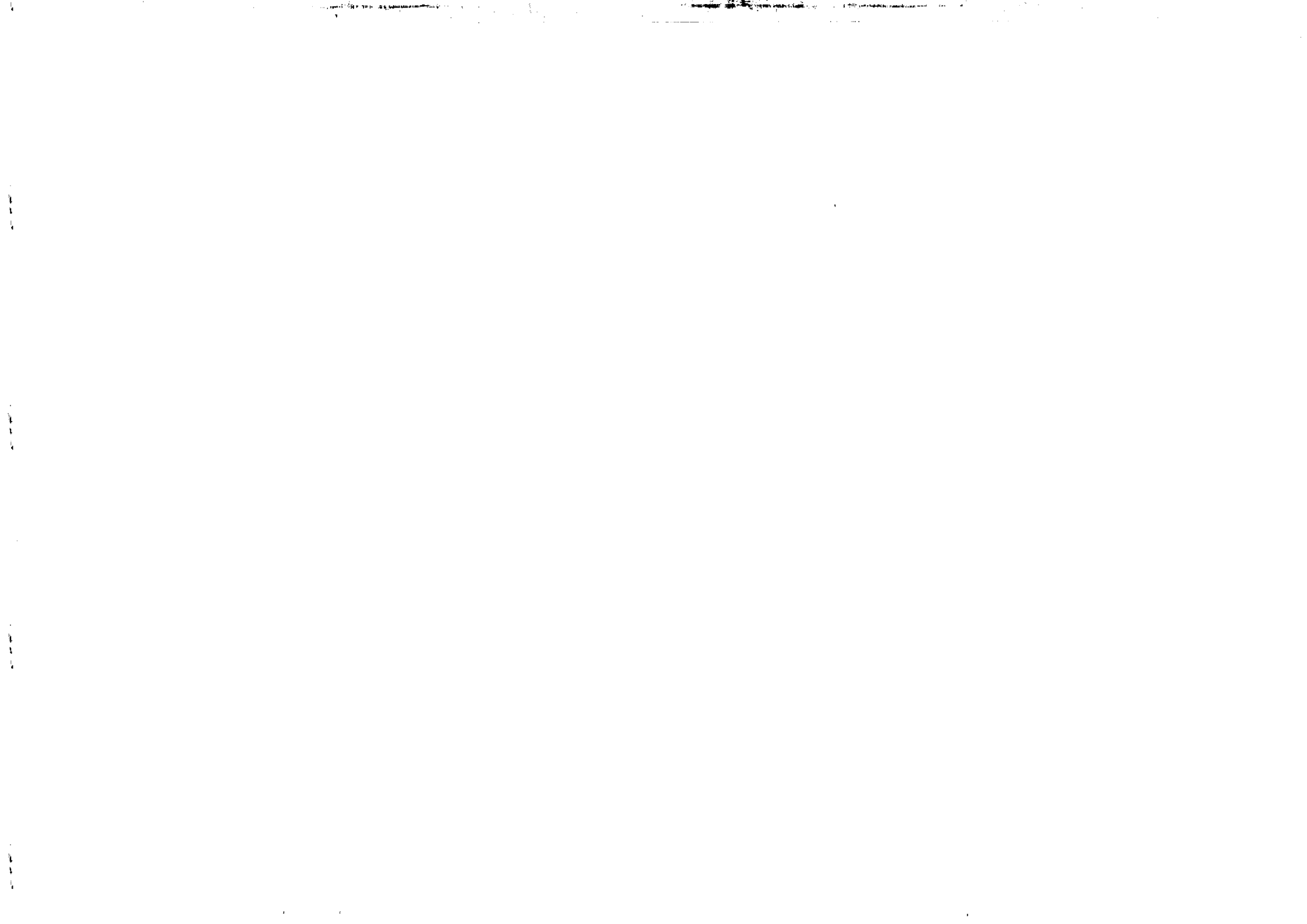
MELTING AND LIQUID STRUCTURE OF POLYVALENT METAL HALIDES

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Abstract. A short review is given of recent progress in determining and understanding liquid structure types and melting mechanisms for halides of polyvalent metals. The nature of the preferred local coordination for the polyvalent metal ion in the melt can usually be ascertained from data on liquid mixtures with halogen-donating alkali halides. The stability of these local coordination states and the connectivity that arises between them in the approach to the pure melt determines the character of its short-range and possible medium-range order. A broad classification of structural and melting behaviours can be given on the basis of measured melting parameters and transport coefficients for many compounds, in combination with the available diffraction data on the liquid structure of several compounds. Correlations have been shown to exist with a simple indicator of the nature of the chemical bond and also with appropriate parameters of ionic models, whenever the latter are usefully applicable for semiquantitative calculations of liquid structure. Consequences on the mechanisms for valence electron localization in solutions of metallic elements into strongly structured molten salts are also briefly discussed.

1. Introduction

In his review article on the electrical properties of unusual ionic melts Hensel [1] contrasted fully ionized molten salts, such as the alkali metal halides or nitrates, with slightly ionized molecular liquids such as $HgCl_2$, AlI_3 or H_2O. He also stressed that increases in density through the application of high pressure drive the self-ionization equilibrium in the latter liquids towards the fully ionized state.

For an illustration of the main theme of the present short review and of its relationship with Hensel's theme, let us contrast the melting behaviours of YCl_3 and $AlCl_3$. The crystal structure of both compounds is the $AlCl_3$-type, that is a layer structure which may be obtained by small distortions from a cubic close packing of chlorines accomodating the trivalent metal ions at octahedral sites. Each layer in its ideal undistorted configuration comprises two triangular lattices of chlorines sandwiching the metal ions into edge-sharing $(YCl_6)^{3-}$ or $(AlCl_6)^{3-}$ octahedra. The breathing mode for octahedral-type coordination of the Y ion by chlorines at $v \sim 260$ cm^{-1} has been observed in Raman scattering experiments on mixed crystals and followed in Y-alkali chloride melts over almost the whole composition range [2]. The $YCl_3 \cdot 3ACl$ melt (with A = alkali) may thus be viewed as containing separate $(YCl_6)^{3-}$ units, with a lifetime which should be quite long as compared with the period of the breathing mode. Some halogen sharing and formation of connectivity are necessary if such relatively long-lived coordination states are to survive with varying composition on the approach to the pure YCl_3 melt.

In pure YCl_3 melting occurs at 994 K with a relatively moderate entropy change ($\Delta S = 7.6$ cal mol^{-1} K^{-1}) and a very small volume change ($\Delta V/V_1 \approx 0.0045$), the ionic conductivity of the melt being relatively modest but still appreciable ($\sigma = 0.39$ Ω^{-1} cm^{-1}). Neutron diffraction experiments on molten YCl_3 show [3] that (i) the coordination number for Cl about Y is about 5.9, (ii) the ratio of the Cl-Cl to Y-Cl bond lengths is approximately equal to that appropriate for ideal octahedral coordination, and (iii) the Faber-Ziman structure factor exhibits a first sharp diffraction peak (FSDP) at scattering wave number $k = 0.95$ Å^{-1}. The presence of a FSDP at $k \approx$ 1 Å^{-1} is a marker of intermediate range order in the melt extending beyond first and second neighbours, as is well known from studies on many strongly structured liquids and glassy materials [4, 5].

In contrast the $(AlCl_4)^-$ coordination is known to be strongly stable in liquid Al-alkali chloride mixtures [6-8]. $AlCl_3$ melts at 466 K with very large changes in entropy and volume ($\Delta S = 18.1$ cal mol^{-1} K^{-1} and $\Delta V/V_1 \approx 0.47$) and the melt has very low electric conductivity ($\sigma = 5 \times 10^{-7}$ Ω^{-1} cm^{-1}) and relatively low shear viscosity ($\eta = 0.36$ cp). From X-ray diffraction experiments the melt is a molecular liquid of Al_2Cl_6 dimers [9]. The melting process may be viewed as driven by a structural phase transition from the $AlCl_3$-type to the $AlBr_3$-type structure, which is formed by chemically saturated molecular dimers [10]. In an ideal Al_2Cl_6 molecule each Al ion is surrounded by a tetrahedron of chlorines and the molecule consists of two tetrahedra sharing a Cl-Cl edge.

As we shall see, the melting mechanisms and liquid structure types of YCl_3 and $AlCl_3$ occupy rather special positions within the series of trivalent metal halides along the path leading from fully ionized melts to slightly ionized molecular melts. From the above discussion of these illustrative examples it is evident that one may draw useful inferences (i) from indirect knowledge of the preferred local coordination for the polyvalent metal ion in the melt on the basis of data on liquid mixtures with halogen-donating alkali halides, and (ii) from measured melting parameters and transport coefficients of the melt. This observation opens the possibility of comparatively examining structural behaviours within broad families of compounds, even though diffraction studies of liquid structure may be available only for a few compounds. The result has been a classification of structural types and the highlighting of correlations with chemical and physical parameters characterizing each compound. The following discussion will review progress made along these lines in recent years.

2. Local coordination of polyvalent metal ions in molten halide mixtures

An alkali halide dissolved into a polyvalent metal halide acts as a halogen donor to break the structural connectivity or the molecular units that may be stable in the pure melt, ultimately

allowing the formation of separate local coordination units for the polyvalent metal ions. The alkali ions further act on local structure mainly through screening by counterions as appropriate in an ionic conducting fluid.

The relevant structural questions are whether the mixture contains "complexes", i. e. negatively charged molecular ions having a lifetime of at least the order of translational and rotational diffusion times ($\approx 10^{-11}$ s), and what are the coordination and the geometry of these complexes. The main alternative possibilities are (i) long-lived fourfold complexes (e. g. for Zn^{2+} [11], Mg^{2+} [12] and Al^{3+} [6-8]), (ii) long-lived sixfold complexes (e. g. for Y^{3+} [2]), and (iii) loose fluctuating coordination (e. g. for Ca^{2+} in $CaCl_2 \cdot 2KCl$, where coexistence of tetrahedral-type and octahedral-type coordinations has been reported from Raman scattering [13]). Some 140 such liquid mixtures have been examined by appropriate experimental probes, involving diffraction in a few cases but mostly Raman scattering, infrared absorption and emission, optical absorption from electronic transitions, and thermodynamic measurements. A classification of the ample evidence on local coordination states in mixtures has been given by Akdeniz and Tosi [14].

General semiempirical approaches to such "structure sorting" problems are well known in solid state physics for the classification of crystal structures in broad families of compounds. In brief, these approaches lead to structural diagrams assembling compounds with similar structure in certain regions of a plane whose coordinates are constructed from parameters of the component elements. In various available classification schemes [15-19], the elemental parameters are radii associated with the valence electron orbitals, which are obtained from first-principles atomic calculations. These elemental parameters correlate to a considerable extent with classical ionic radii, although they carry information not only on geometric core sizes but also on chemical bonding properties. More recently, Pettifor [20] has proposed a chemical scale of the elements which is aimed at the same purpose in a more empirical viewpoint, though incorporating recent progress in understanding the cohesion of bulk solids from first-principles calculations.

These structure-sorting approaches have been successfully adapted to the liquid structure problem at hand [14]. As the best example Figure 1 reports the structural diagram obtained for liquid mixtures of polyvalent metal and alkali metal halides on the basis of Pettifor's chemical scale χ of the elements. The diagram mainly refers to a concentration c of polyvalent metal halide that would *a priori* favour fourfold coordination, i.e. c = 1/3 for divalent ions and c = 1/2 for trivalent ions.

In constructing the structural diagram in Figure 1, structural coordinates have been obtained for each M-A(X) liquid mixture from the elemental property χ as

$$X_{M-A(X)} = \chi_M - \chi_A \quad , \quad Y_{M-A(X)} = \chi_M + \chi_A - 2\chi_X \tag{1}$$

(with M = polyvalent metal, A = alkali and X = halogen). Each mixture is represented in the diagram by an appropriate symbol distinguishing, on the basis of the available evidence, the stability of fourfold coordination as strong (dots), marginal (circles) or absent (lozenges). The marginal stability class includes cases of recognized coexistence between fourfold and more highly coordinated states, as well as systems for which the available evidence gives ambiguous indications. The plane in Figure 1 can now be partitioned by lines into various regions, distinguishing (from top right to bottom left) (i) strong stability of fourfold coordination, (ii) strong stability of sixfold coordination, and (iii) loose fluctuating coordination. The locations of the separation lines between these classes of structural behaviour are set (i) by the Cr-alkali chloride systems, the Cr ion being known from electronic absorption spectra to be tetrahedrally coordinated in the divalent state and octahedrally coordinated in the trivalent state [21], and (ii) by the Y-alkali and Ca-alkali chloride systems, as discussed earlier in this review.

The roles of the halogen partner and of the alkali counterion can also be seen from Figure 1. Chlorides, bromides and iodides have closely related behaviours, but the fluorides require specific discussion. For instance, while the $(AlCl_4)^-$ unit has strong stability in Al-alkali chloride mixtures, the Raman spectrum of molten $(AlF_3)_c \cdot (NaF)_{1-c}$ and other Al-alkali fluoride mixtures gives evidence for a gradual conversion of $(AlF_4)^-$ units into $(AlF_6)^{3-}$ and possibly $(AlF_5)^{2-}$ units as c is lowered below 0.5 [22, 23]. The Raman data also indicate a role of the alkali counterions in the equilibrium, the $(AlF_4)^-$ unit being destabilized on replacing Na by Li and stabilized on replacing Na by K. More generally, Li counterions appear to destabilize

molecular-ion bound states, as can be seen from Figure 1. The underlying effect is ionic-conductor screening, as will be discussed immediately below.

Within the general frame provided by structure sorting, a number of liquid mixtures are of special interest and deserve microscopic evaluation. To convey the flavour of such theoretical work in a case where a classical model of ionic liquids is already helpful, one may ask whether tetrahedral $(CaCl_4)^{2-}$ complexes will form and persist over relatively long times in the aforementioned $CaCl_2 \cdot 2KCl$ melt. This question may be tackled theoretically by evaluating by statistical mechanical methods the reaction equilibrium $(CaCl_4)^{2-} \leftrightarrow Ca^{2+} + 4Cl^-$ in the dense ionic medium [24]. The dissociation free energy (selfconsistently dependent on the concentration of complexes) is determined by a balance between the binding free energy of the isolated complex and the change in the interaction free energy of the components of the liquid on dissociation of a complex.

Insofar as the binding of $(CaCl_4)^{2-}$ is mainly ionic and the effect of the liquid medium is primarily the screening of $(CaCl_4)^{2-}$ by free K^+ ions, the balance between the above free energies is inversely proportional to a balance between the cation-anion distance d within a complex and the screening length L of the liquid. Appeal to Mott's criterion for the stability of a bound state in a conducting fluid then suggests that complexes are stable if the ratio L/d is larger than some critical value [25]. A statistical mechanical treatment estimates L for various melts and indicates that the critical value of L/d is approximately 1.6 for molten salt mixtures. Table 1 shows that this critical ratio separates the alkaline earth - alkali chlorides into complex forming (Be and Mg) and non-forming (Sr and Ba), with fluctuations between fourfold and higher coordinations being expected for Ca. The results of this stability sorting criterion are in agreement with the available Raman scattering evidence [13]. Table 1 includes also the Al-alkali chloride mixtures as a further example of strongly stable tetrahedral coordination.

In summary, ample experimental evidence is available in the literature on the type and stability of the local coordination for polyvalent metal ions in molten mixtures of their halides with alkali halides. Dissociation of tetrahedral halocomplexes in good ionic systems may be viewed as a classical Mott problem of bound-state stability in a conducting liquid matrix. More generally, established methods for crystal structure sorting can be adapted to construct structural coordinates for molten salt mixtures from properties of the component elements, which separate out systems with long-lived fourfold or sixfold coordination and distinguish between these.

3. Melting mechanisms and liquid structure types

It was pointed out in section 1 that the preferred local coordination of Y^{3+} (octahedral-type) and Al^{3+} (tetrahedral-type) in mixtures of their chlorides with alkali chlorides persists up to the pure YCl_3 or $AlCl_3$ melt. The consequences on the melting mechanism of these compounds and on their liquid structure are (i) melting from an ionic crystal into an ionic liquid with residual connectivity and intermediate range order for YCl_3, and (ii) melting from an ionic crystal into a molecular liquid of Al_2Cl_6 dimers for $AlCl_3$. The two different melting mechanisms are reflected in the respective values of the melting parameters (entropy and volume change) and of transport coefficients (ionic conductivity and shear viscosity in the melt) for the two compounds.

This type of analysis of macroscopic data has recently been extended to a large number of halides of monovalent, divalent and trivalent metal ions [26]. Some examples are reported for chlorides in Table 2. The examples have been chosen to illustrate the various types of melting mechanism that have been identified from the macroscopic evidence in combination with the available diffraction studies of liquid structure.

Before proceeding to a detailed discussion of Table 2, it is useful to recall an empirical relationship that has been proposed [27] between the entropy change ΔS and the relative volume change $\Delta V/V$ across melting. It reads

$$\Delta S = n R \ln 2 + \gamma C_v \frac{\Delta V}{V} \qquad (2)$$

where n is the number of atoms in a formula unit, R the gas constant, γ the Grüneisen parameter and C_v the heat capacity. Insofar as γ and C_v take similar values for similar systems in corresponding states, the above equation implies an approximate linear relationship between the

melting parameters ΔS and $\Delta V/V$, extrapolating for $\Delta V/V \to 0$ to a constant value of ΔS per atom. As can be seen from Figure 2, the relationship (2) is indeed satisfied [26] by a large number of halides of monovalent, divalent and trivalent metal ions (shown in the Figure by empty circles, squares and triangles, respectively). However, several systems can be found which have a deficit in entropy of melting relative to the "norm", as shown in Figure 2 by filled symbols. These exceptions are associated with special melting mechanisms as will be discussed below.

3.1. Monovalent metal halides

Let us now return to Table 2. The data for NaCl in the first row of the Table are representative of all alkali halides and are typical of loosely coordinated ionic melts. Their main structural characteristics arise from excluded volume effects and relative Coulomb ordering of the two component species (see for example Rovere and Tosi [28]). The melting parameters of all alkali halides, as well as those of AgCl, TlBr, TlI and InCl, closely obey the relationship (2) with $n = 2$.

Melting in CuCl, on the other hand, is preceded by disordering on the copper sublattice, as signalled by the fact that the ionic conductivity attains in the high temperature crystal values of magnitude similar to those of the melt. This compound shows a large deficit in the entropy of melting, which is evidently reflecting the previous release of entropy in the disordering of the cationic component of the crystal on the approach to melting. Similar behaviours are shown by AgBr and AgI. The measured liquid structure of CuCl shows that the relative short-range order of the Cu^+ ions in the melt is very low [29, 30]. Thus, traces of the fast-ion conducting state in the hot crystal persist in the liquid phase near freezing.

3.2. Divalent metal halides

Among divalent metal chlorides $SrCl_2$ shows again a deficit in the entropy of melting, which is associated with disordering of the anion sublattice in the high temperature crystal through a continuous transition to a superionic state. A relatively high dynamic concentration of anionic crystal defects is generated across the transition. The liquid structure of $SrCl_2$ is still dominated by the short-range order in the system of Sr^{2+} ions, while a poorer degree of order is observed in the system of chlorines [31]. Similar behaviours are shown by $SrBr_2$ and $BaCl_2$, except that the fast-ion conducting state in the crystal is attained through a structural phase transition.

$CaCl_2$ and $MgCl_2$ in the next two rows of Table 2 are representative of many other divalent metal halides, whose melting parameters obey the relationship (2) with $n \approx 3$. Their crystal structures (of three-dimensional and layer-type character, respectively) can be described as formed from slightly distorted close packings of the halogens, inside which the metal ions occupy interstitial sites in an octahedral-type coordination. The liquid structure, as determined by neutron diffraction for $CaCl_2$ [32] and $MgCl_2$ [33], shows loose ionic coordination accompanied by some intermediate range order. Remnants of two-dimensional structural characters have been noticed in molten $MgCl_2$ [34].

$HgCl_2$, as well as $HgBr_2$ and HgI_2, in their high temperature crystal structures are instead best viewed as molecular crystals composed of monomeric formula units having linear shape. The liquid phase shows very low ionic conductivity and "normal" viscosity (see Table 2) and accordingly these melts are commonly described as slightly ionized molecular liquids. The entropy and volume changes of these compounds on melting essentially conform to the "norm" given by eqn (2). It seems likely that the linear shape of the monomer prevents the formation of strong intermolecular correlations in the melt, contrary to the case of molecular liquids formed by trihalides (see below).

$ZnCl_2$ has drawn particular interest in the literature from the fact that it can be brought to a glassy state by rapid cooling from the melt. Melting occurs from a crystal structure formed by a three-dimensional network of corner-sharing tetrahedral units centred on the metal ions, and leads to a melt with very low ionic conductivity and very high viscosity. As is known from neutron diffraction experiments [35], the melting process preserves a stable tetrahedral coordination of the metal ions by chlorines and yields a liquid in a state of pronounced intermediate range order. A detailed discussion of this state of order in molten and glassy 2:1 binary compounds and

of the attendant FSDP in the scattering pattern has been given recently by Salmon [36]. A network-like structure built from corner-sharing tetrahedral coordinations of the metal ions implies that the Cl-Cl and Zn-Zn first neighbour distances are closely similar and equal to about $3.7 \div 3.8$ Å. In contrast, the metal-metal first neighbour distance in a strongly ionic melt such as $SrCl_2$ is approximately 5 Å and very different from the Cl-Cl one.

$ZnCl_2$ shows a very large deficit in the entropy of melting. It appears that melting into a strongly structured network-like liquid does not absorb the full "normal" amount of entropy. The deficit should be gradually made up as the structure of the melt loosens on further heating in the liquid state. Similar behaviours are shown by BeF_2 and $BeCl_2$. BeF_2 is again a glass-former with a three-dimensional network structure from corner-sharing tetrahedra, whereas for $BeCl_2$ the local tetrahedral coordination leads through edge-sharing to the chain-like "fibrous SiS_2" crystal structure.

3.3. Trivalent metal halides

$LaCl_3$ in the next column in Table 2 is representative of the lanthanide metal trihalides crystallizing in the closely related UCl_3 or $PuBr_3$ structures. Each metal ion is coordinated in the crystal by six halogens at the corners of a trigonal prism and by three further halogens at somewhat larger distances. The melting parameters obey the relationship (2) with a value of n which apparently is somewhat larger than 4. Studies of these melts by X-ray diffraction [37] indicate a rather loose ionic-type liquid structure, with essentially sixfold coordination of the metal ions by halogens and a metal-metal first neighbour distance of approximately 5 Å. As already noted, this value is typical of strongly ionic polyhalide melts and indeed is reproduced by liquid structure calculations in an ionic model for trihalides [38].

The crystalline and liquid structures of YCl_3 and its melting mechanism have already been discussed in section 1. This compound differs from $LaCl_3$ and other lanthanide metal trihalides only in matters of quantitative degree: octahedral-type coordination of the metal ions appears to be somewhat more stable and some amount of intermediate range order is clearly present in the melt. The low value of the entropy of melting is related to the very small value of the volume change on melting as indicated by eqn (2). $DyCl_3$ crystallizes in the same $AlCl_3$-type structure and appears to have melting and liquid-state behaviours which are very similar to YCl_3.

As already discussed in section 1, the melting mechanism of $AlCl_3$ has the distinguishing feature of being accompanied by an ionic-to-molecular phase transition. An interpretation of this behaviour, contrasted with those shown by $LaCl_3$ and YCl_3, will be presented in section 3.4 below. $InCl_3$, which also crystallizes in the $AlCl_3$-type structure and melts with a very large volume change, may present another instance of such melting mechanism. Indeed, the In_2Cl_6 dimer is known to be stable in the vapour phase. However, the melting temperature and the ionic conductivity of $InCl_3$ ($T_m = 859$ K and $\sigma = 0.42 \ \Omega^{-1} \ cm^{-1}$) are appreciably higher than those of $AlCl_3$, suggesting partial thermal breakage of molecular units in the melt.

For other trivalent metal halides, such as $GaCl_3$, $BiCl_3$ and $SbCl_3$ as reported in the last three rows of Table 2, the presence of molecular units can already be recognized in the crystal structure. Excepting $BiCl_3$, the melting process brings such compounds from molecular crystals into slightly ionized molecular liquids characterized by very low ionic conductivity. In the case of $GaCl_3$, as well as for $AlBr_3$ and AlI_3, the crystal structures are formed by arranging into layers dimeric units shaped as an edge-sharing double tetrahedron. For $BiCl_3$ and $SbCl_3$, on the other hand, the crystal structures are three-dimensional packings of chains obtained from stacking monomers which are shaped as trigonal pyramids with the metal ion at the apex. The liquid structure of $SbCl_3$ has been studied by neutron and X-ray diffraction [39, 40]. It can be described as arising from discrete monomeric units with strong intermolecular correlations, leading to an associated molecular liquid. The chlorines are in a distorted octahedral arrangement around the metal ions, as would result from stacking monomeric units in an umbrella configuration. Excepting again $BiCl_3$, all these compounds show a deficit in the entropy of melting relative to the "norm" given for trihalides in eqn (2). This may be associated with the preservation of molecular units as basic constituents with strong intermolecular correlations, rather than with a network-like structure as in $ZnCl_2$ or BeF_2.

In comparison with other molecular-type trihalides, $BiCl_3$ melts at somewhat higher

temperature and shows an appreciable ionic conductivity and a very high viscosity in the melt (see Table 2). These properties suggest that, if monomers still are basic constituents of the liquid phase, they are strongly interacting through relatively fast exchanges of the chlorines. A neutron diffraction study of molten $BiCl_3$ by M.-L. Saboungi and D. L. Price (to be published) indicates a melt with an ionic-type structure, characterized by a fairly stable local coordination of the halogens around the metal ions and by a faint trace of intermediate range order. The liquid structure of $BiCl_3$ appears in fact to be qualitatively similar to that of BiI_3, as reported by Ichikawa and Matsumoto [41]. The latter compound crystallizes in the ionic-type $FeCl_3$ structure and has an ionic conductivity in the melt similar to that of $BiCl_3$.

In summary, while the crystal structure types of trivalent metal halides may be broadly classified into ionic and molecular, in addition to melting mechanisms of ionic-to-ionic type (lanthanide metal halides and YCl_3) and of molecular-to-molecular type (e.g. $GaCl_3$ and $SbCl_3$) one may identify melting mechanisms of ionic-to-molecular type ($AlCl_3$ and possibly $InCl_3$) and of molecular-to-ionic type ($BiCl_3$). Only for the molecular-to-molecular melting mechanism does one find evidence for a deficit in the entropy of melting relative to the "norm" given by eqn (2).

3.4. Liquid structure for trihalides in an ionic model

Each compound in Table 2 is accompanied by the value of Pettifor's chemical activity parameter χ_M for the metallic element entering it. There is a good correlation between the values of this parameter and the various melting and liquid structure behaviours that have been discussed in the preceding parts of this section. Increasing values of χ_M crudely correspond to an increasing role of chemical bonding relative to pure Coulomb interactions between closed-shell ions. In view of the discussion given earlier in section 2, the correlation also extends to the preferred local structure of the metals ions in halogen-enriched mixtures.

A microscopic analysis of the relationship between the character of the local coordination and the intermediate range order in the melt has been given very recently by H. Tatlipinar, Z. Akdeniz, G. Pastore and M. P. Tosi (to be published) in an ionic model for molten trihalides. The basic parameter of the model fluid is the ionic radius R_M of the trivalent metal ion, which is

allowed to span the range from La^{3+} ($R_M = 1.42$ Å) to Al^{3+} ($R_M \approx 0.82$ Å). The model includes Coulombic interactions and soft-sphere overlap repulsions, incorporating in its parameters the results of an analysis of preferred coordinations in liquid halide mixtures [42], and is solved for liquid structure in the hypernetted chain approximation.

The main result of the calculations is to demonstrate the correlation that exists between the formation of a strong local coordination of the polyvalent metal ions and the growth of intermediate range order in the melt. The latter may also be induced by strong interactions between local molecular-like coordinations in a dense liquid and is not necessarily associated with a covalent network structure of the liquid. This correlation is shown in Figure 3, reporting the average running coordination number $N_{+-}(r)$ of a metal ion for three values of R_M at fixed liquid density and temperature, and in Figure 4, showing the corresponding number-number structure factor $S_{NN}(k)$. These quantities are defined as

$$N_{+-}(r) = 4\pi n_- \int_0^r g_{+-}(r') \, r'^2 dr' \tag{3}$$

and

$$S_{NN}(k) = \frac{1}{4}\left[S_{++}(k) + 2\,(3)^{1/2} S_{+-}(k) + 3\,S_{--}(k) \right] \,, \tag{4}$$

where n_- is the number density of halogens, $g_{+-}(r)$ is the metal-halogen radial distribution function and $S_{ij}(k)$ are the partial structure factors.

It is seen from Figure 3 that at $R_M = 1.42$ Å the number of chlorine first neighbours about a trivalent metal ion is of order 7 and there is appreciable exchange of chlorines between the first and second neighbour shells. The plateau in $N_{+-}(r)$ decreases in height and flattens out with decreasing R_M, until at the opposite end of the range of R_M ($R_M = 0.82$ Å) the number of chlorines about the trivalent metal ion reaches a value of about 4, the local average topology being of distorted tetrahedral type, and the exchange between the first neighbour shell and the rest of the liquid is almost completely suppressed. The corresponding number of trivalent metal ions about a chlorine is directly obtained from the composition of the melt as being about 4/3.

The value 4/3 is the one appropriate to chlorines in the Al_2Cl_6 dimer.

The number-number structure factor $S_{NN}(k)$ is especially significant in regard to the formation of order at intermediate range in the melt, which is signalled by the presence of a FSDP in this structural function at $k \approx 1$ Å^{-1} [4, 5]. It is seen from the FSDP in Figure 4 that intermediate range order is very strong at the lower end of the range of R_M and progressively weakens as R_M increases. This behaviour with ionic size parallels the decreasing stability shown for the local coordination structure of the metal ions in Figure 3. A strong and stable local structure is clearly a prerequisite for the formation of the medium-range connectivity which is reflected in a prominent FSDP.

The structure of the model liquid at $R_M = 0.82$ Å is representative of molten $AlCl_3$ in a partly ionized state as may be realized at relatively high density and temperature. Traces of Al_2Cl_6 dimers may nevertheless be recognized in the calculated liquid structure. An appreciable decrease in density further strengthens the stability of the first neighbour shell, leaving an essentially fourfold coordination of the trivalent ions by chlorines of distorted tetrahedral type and an appreciable degree of intermediate range order. It also reduces the Cl-Cl coordination number to a value slightly below 4 (the value appropriate to an ideal Al_2Cl_6 dimer being 11/3) and reduces the metal-metal coordination number to approximately unity. Thus the decrease in density strengthens the resemblance of local structure in the model fluid to that of a fluid of Al_2Cl_6 dimers. The model fluid at low density appears to be composed of distorted dimers, and by a suitable decrease in temperature can be brought to an instability against phase separation into two phases of different density. The intermolecular interactions are mainly multipolar in character and weaken rapidly with decreasing density, thus stabilizing the vapour phase.

The detailed scenario that can be built in an ionic model by allowing the metal ion size to change over the range from La^{3+} to Al^{3+} is thus in full agreement with the observed trends that have been discussed earlier in this section. Covalent contributions to the bonding would modify the details and presumably sharpen the transitions between different types of liquid structure, but the overall picture that is obtained in a simple ionic model appears to be essentially correct.

4. Concluding remarks on metal - molten salt solutions

Solutions of metals in molten salts are among the several classes of liquid systems which undergo a transformation from a nonmetallic to a metallic state on changing some thermodynamic variable. In concluding this short review on polyvalent metal halide melts, it seems appropriate to briefly point out the consequences of a strong structure for the pure molten salt in regard to its behaviour on metal addition.

In alkali - alkali halide solutions above the consolute critical temperature, the electric conductivity increases gradually as the nature of the states for electronic carriers evolves with increasing metal concentration [43]. At high metal dilution single electrons are trapped in localized states partaking of F-centre and polaron character, in the sense that localization occurs at favourable fluctuations of potential via a substantial rearrangement of the local liquid structure. Such single-electron states are next rapidly replaced by spin-paired electron states, which further appear to evolve towards small fluctuating clusters of metal. The transition to a metallic state for the liquid as a whole is most strikingly signalled by a dielectric anomaly and appears to develop at metal concentrations appreciably below the critical concentration for demixing.

Much less attention has been given to electron localization in metal - molten salt solutions involving polyvalent metals, a notable exception being the Bi - Bi halides [44]. A broad trend can already be recognized from the available electric conductivity data [45]. Starting from the alkaline earths as being immediately more chemically active than the alkalis, the observed behaviour of the conductivity with metal concentration appears to correlate with the character of the liquid structure of the pure alkaline earth chloride. Thus, the conductivity in Ca - CaX_2 systems (X denoting a halogen) increases much more slowly with metal addition than in Sr - SrX_2 or Ba - BaX_2 systems. Eventually, as one proceeds through polyvalent metals along a path set by Pettifor's chemical activity scale, electron localization by reconstruction of local liquid structure and of chemical bonding will result. As an example one may mention the Hg - $HgCl_2$ system, which may be viewed as a nonmetallic mixture of $HgCl_2$ and Hg_2Cl_2 in the composition range up to that of the 'subhalide' Hg_2Cl_2 and as an Hg - Hg_2Cl_2 solution at still higher metal concentration [44].

A microscopic model for processes of structure breaking accompanied by the formation of reduced oxidation states has recently been evaluated [46] in the specific case of dilute solutions of sodium metal in molten cryolite ($AlF_3 \cdot 3NaF$). On assuming that the sodium metal enters molten cryolite in the form of Na^+ ions and electrons, the calculations demonstrate how these added components break up the structure of the ionic melt to yield electron localization by the formation of Al ions in reduced valence states. It is found that with increasing Na metal content the equilibrium between $(AlF_6)^{3-}$ and $(AlF_4)^-$ shifts in favour of the latter, while at the same time Al^{3+} ions are released into the melt and bind the available electrons to form Al^{2+} and Al^+ ions. Eventually the latter oxidation state becomes the most stable one and the $(AlF_4)^-$ complex is also destabilized. This scenario is consistent with macroscopic observations on the chemical products resulting from adding metals to molten cryolite.

The specific example of metal - cryolite solutions is illustrative of what one may expect to be a rather general feature of electron localization in strongly structured molten salts. Electron localization involves structure breaking and the required expense of free energy is balanced through reconstruction of chemical bonding. Obviously, the formation of lower oxidation states for the polyvalent metal ion will broaden the nonmetallic range of the solution and shift the liquid miscibility gap towards the metal-rich side of the phase diagram.

Acknowledgements

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Table 1. Range of L/d for polyvalent metal - alkali chloride mixtures on varying the alkali A from Li to Cs

	$AlCl_3 \cdot ACl$	$BeCl_2 \cdot 2ACl$	$MgCl_2 \cdot 2ACl$	$CaCl_2 \cdot 2ACl$	$SrCl_2 \cdot 2ACl$	$BaCl_2 \cdot 2ACl$
L/d	1.74÷1.80	1.79÷1.85	1.66÷1.72	1.56÷1.61	1.52÷1.57	1.48÷1.53

Table 2. Properties of metal chlorides

Salt	χ_M	Structure [a]	T_m (K)	ΔS (e.u.)	$\Delta V/V_1$ [b]	$\sigma\,(\Omega^{-1}cm^{-1})$	η (cp)
NaCl	0.40	NaCl	1074	6.30	0.28	3.6	1.0
CuCl	1.20	Wurtzite	696	2.43	0.16	3.7	4.1
$SrCl_2$	0.55	CaF_2	1146	3.44	0.11	2.0	3.7
$CaCl_2$	0.60	$CaCl_2$	1045	6.44	0.043	2.0	3.4
$MgCl_2$	1.28	$CdCl_2$	980	9.74	0.28	1.0	2.2
$HgCl_2$	1.32	$HgCl_2$	554	9.11	0.21	3×10^{-5}	1.6
$ZnCl_2$	1.44	$ZnCl_2$	570	4.09	0.14	1×10^{-3}	4×10^3
$LaCl_3$	0.705	UCl_3	1131	11.49	0.16	1.3	6.7
YCl_3	0.66	$AlCl_3$	994	7.56	0.0045	0.39	--
$AlCl_3$	1.66	$AlCl_3$	466	18.14	0.47	5×10^{-7}	0.36
$GaCl_3$	1.68	$GaCl_3$	351	7.84	0.17	2×10^{-6}	1.8
$BiCl_3$	2.04	$BiCl_3$	507	11.20	0.18	0.38	41.0
$SbCl_3$	2.08	$SbCl_3$	346	8.96	0.17	2×10^{-4}	--

[a] Structure of high temperature crystal phase.

[b] Relative difference between the volume of the liquid at T_m and that of the solid at room temperature, the volume of the solid at T_m being in some cases unknown.

Figure captions

Figure 1. Stability map for fourfold coordination in liquid M-A(X) mixtures. The label (Cl) has been omitted for the chlorides. The break in the vertical scale refers to the fluoride systems. From Z. Akdeniz and M. P. Tosi [14].

Figure 2. Relations between the entropy of melting ΔS (in cal mol^{-1} K^{-1}) and the relative volume change $\Delta V/V_1$ for halides of monovalent, divalent and trivalent metals. Empty circles, squares and triangles represent those compounds that conform to eqn (2). The filled symbols represent systems showing strong deviations from eqn (2). These are, in order of increasing $\Delta V/V_1$ for each valence state: circles, the fast-ion conductors AgI, AgBr and CuCl; squares, the fast-ion conductors $SrCl_2$, $SrBr_2$ and $BaCl_2$; lozenges, the network formers BeF_2, $ZnCl_2$ and $BeCl_2$; and triangles, the associated molecular systems $AlBr_3$, AlI_3, $GaCl_3$, $SbCl_3$ and $SbBr_3$. From Z. Akdeniz and M. P. Tosi [26].

Figure 3. Average running coordination number of a metal ion by chlorines in an ionic model for molten trihalides, as a function of distance r in units of the mean ion-sphere radius a = 1.96 Å. Dotted curve is for $LaCl_3$ ($R_M \approx 1.42$ Å), dashed curve for YCl_3 ($R_M \approx 1.2$ Å) and full curve for $AlCl_3$ ($R_M \approx 0.82$ Å). The density and temperature of the melt refer to YCl_3 near freezing ($\rho = 0.0316$ Å^{-3} and T = 1020 K).

Figure 4. Number-number structure factor in an ionic model for molten trihalides. The symbols are as in Figure 3.